

# Long term degree of conversion of two bulk-fill composites

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Par, Matej; Lapaš Barišić, Matea; Gamulin, Ozren; Pandurić, Vlatko; Španović, Nika; Tarle, Zrinka

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Matej Par<sup>1</sup>, Matea Lapas-Barisic<sup>1</sup>, Ozren Gamulin<sup>2,3</sup>, Vlatko Panduric<sup>4</sup>, Nika Spanovic<sup>1</sup>, Zrinka Tarle<sup>4</sup>

## Dugoročna naknadna polimerizacija dvaju „*bulk-fill*” kompozita

### Long Term Degree of Conversion of two Bulk-Fill Composites

<sup>1</sup> Privatna stomatološka ordinacija, Zagreb

*Private Dental Practice, Dankovečka 9, Zagreb, Croatia*

<sup>2</sup> Zavod za fiziku i biofiziku Medicinskog fakulteta Sveučilišta u Zagrebu

*Department of Physics and Biophysics, School of Medicine, University of Zagreb, Salata 3b, Zagreb, Croatia*

<sup>3</sup> Znanstveni centar izvrsnosti za napredne materijale i senzore, istraživačka jedinica Novi funkcionalni materijali, Bijenička cesta 54, Zagreb, Hrvatska

*Center of Excellence for Advanced Materials and Sensing Devices, Research Unit New Functional Materials, Bijenička cesta 54, Zagreb, Croatia*

<sup>4</sup> Zavod za endodonciju i restaurativnu dentalnu medicine Stomatološkog fakulteta Sveučilišta u Zagrebu

*Department of Endodontics and Restorative Dentistry, School of Dental Medicine, University of Zagreb, Gundulićeva 5, Zagreb, Croatia*

#### Sažetak

**Svrha:** Istražiti dugoročan razvoj stupnja konverzije (SK) dvaju tekućih *bulk-fill* kompozita. **Materijali i postupci:** Tetric EvoFlow Bulk Fill (TEFBF) i SDR izabrani su zbog posebnosti u sastavu koje omogućuju smanjenje translucencije tijekom polimerizacije i manju brzinu polimerizacije. SK je izmjeren FT-Ramanovom spektroskopijom nakon 0 i 24 sata te 7 i 30 dana poslije svjetlosne aktivacije. Naknadna polimerizacija analizirana je mješovitim modelom ANOVA-e i parcijalnom eta-kvadrat statistikom. **Rezultati:** Izmjeren je SK u rasponu od 61,3 do 81,1 posto kad je riječ o TEFBF-u i od 58,9 do 81,6 posto za SDR. Početne (0 sati) vrijednosti SK-a bile su značajno niže na dubini od 4 mm nego li na onoj od 1 mm (4,9 % – SDR i 11,1 % – TEFBF). Oba materijala pokazala su značajan porast SK-a nakon svjetlosne aktivacije – do 16,4 posto TEFBF i 20,6 posto SDR. Naknadni porast SK-a ovisio je o dubini, kad je riječ o TEFBF-u, ali ne i o SDR-u. Naknadni porast SK-a zabilježen je tijekom 24 sata pri uporabi TEFBF-a i sedam dana pri uporabi SDR-a. **Zaključak:** Pri uporabi nekih *bulk-fill* kompozita bilo je za postizanje konačnoga SK-a potrebno dulje vrijeme od uobičajeno prihvaćenog razdoblja od 24 sata. To se može pripisati izmjenama u sastavu koje proizvođači najčešće ne otkrivaju. Rezultati sugeriraju da istraživanja koja se uobičajeno obavljaju 24 sata nakon polimerizacije mogu podcijeniti neka svojstva *bulk-fill* kompozita, ako ona ovisе o spororastućem SK-u. Reaktivni spojevi također mogu biti dostupni za otpuštanje iz restoracije tijekom duljeg razdoblja s mogućim implikacijama na biokompatibilnost.

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#### Adresa za dopisivanje

Privatna stomatološka ordinacija  
Dankovečka 9, 10000 Zagreb  
mpar@inet.hr

#### Gljučne riječi

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#### Uvod

Fotopolimerizaciju dentalnih kompozita obilježava kompleksna kinetika i ograničena pokretljivost reaktivnih spojeva tijekom rasta i umrežavanja polimernih lanaca (1). Iako se veći dio polimerizacije događa tijekom svjetlosne aktivacije koja u praksi uobičajeno traje oko 20 sekunda, naknadna polimerizacija nastavlja se sporo i nakon što je osvjetljavanje završeno (2). Tu pojavu uzrokuje smanjena brzina polimerizacije zbog znatnog porasta viskoznosti reakcijskog medija. Vrlo niska pokretljivost usporava brzinu reakcije za nekoliko redova veličine (3), iako je znatna količina reaktivnih spojeva (slobodnih radikala i metakrilatnih monomera) još prisutna (4). Zato se naknadna polimerizacija nastavlja s vrlo niskom i padajućom brzinom, sve dok porast viskoznosti potpuno ne imobilizira preostale reaktivne spojeve. To uzrokuje završetak polimerizacije prije nego što su reaktanti potpuno potrošeni – za dentalne kompozite tipično pri SK-u od 60 do 80 posto (1, 5, 6). Općenito se smatra da naknadna polimerizacija završava unutar 24 sata nakon svjetlosne aktivacije (7 – 9). Iako se u literaturi eksplicitno ne ističe da poli-

#### Introduction

The polymerization reaction of dental composites features complex kinetics and is limited by mobility restrictions imposed on reactive species during the growth and crosslinking of polymeric chains (1). Although most of the polymerization occurs during the light curing, commonly lasting for about 20 s in clinical practice, the post-cure polymerization slowly furthers after the light curing has ended (2). This phenomenon is caused by the reduction of polymerization rate due to an immense increase in viscosity of the reaction medium. Very low mobility causes the reaction rate to drop for several orders of magnitude (3) while the considerable amounts of reactive species (free radicals and methacrylate monomers) are still available (4). Thus the post-cure polymerization continues at very low and decreasing rate, until the viscosity increase completely immobilizes the remaining reactive species. This causes the polymerization to stop before the reactants are completely consumed, for dental composites typically at the DC values of 60-80% (1, 5, 6). The post-cure polymerization is generally considered to be completed

merizacija završava unutar 24 sata, to se implicitno sugerira u mnogobrojnim istraživanjima *in vitro* provedenima nakon razdoblja starenja od 24 sata koje se smatra dostatnim za stabilizaciju promjena u strukturi polimerne mreže radi naknadne polimerizacije (7, 8, 10 – 13). Naknadna polimerizacija poslije 24 sata nije dovoljno istražena – postoji samo jedna studija u kojoj je opisan porast SK-a tijekom 30 dana nakon svjetlosne aktivacije za uzorke aktivirane niskim energijama zračenja (14). Druga studija sugerirala je naknadnu polimerizaciju dulju od 24 sata mjerenjem postupnog porasta tvrdoće do sedam dana (15).

Nova generacija dentalnih kompozita nazvanih *bulk-fill* nedavno je predstavljena na tržištu i sve je prihvaćenija jer omogućuje kraći i jednostavniji klinički postupak. *Bulk-fill* kompoziti proizvedeni su za postavljanje u slojevima od 4 do 5 mm, za razliku od onih konvencionalnih koji omogućuju maksimalnu debljinu sloja od 2 mm. Ovo je omogućeno modifikacijom dvaju glavnih čimbenika koji ograničavaju debljinu kompozitnog sloja – polimerizacijskog stresa i niske translucencije (16, 17). Polimerizacijski stres ublažen je smanjenjem modulusa elastičnosti (13), a translucencija je poboljšana nižim udjelom punila i većim dimenzijama čestica (17). Osim navedenih promjena, *bulk-fill* kompoziti se, prema temeljnom kemijskom sastavu, ne razlikuju znatno od konvencionalnih. Kao temelj zadržali su fotopolimerizirajuću mješavinu bifunkcionalnih metakrilatnih monomera i silanizirana staklena punila. Ipak, kod nekih *bulk-fill* kompozita primijenjen je inovativan pristup u poboljšanju kliničke izvedbe. Konkretno, Tetric EvoFlow Bulk Fill (TEFBF) tijekom polimerizacije mijenja translucenciju od 28 do 10 posto kako bi oponašao dentinski opacitet i time pridonio estetskom izgledu (18). Drugi primjer je SDR koji sadržava patentiranu smolu temeljenu na uretan-dimetakrilatu u čije su molekule ugrađene fotoaktivne skupine koje kontroliraju kinetiku polimerizacije i usporavaju razvoj polimerizacijskog stresa (19). Navedene modifikacije mogu kratkoročno (tijekom svjetlosne aktivacije) i dugoročno (nakon svjetlosne aktivacije) utjecati na kinetiku polimerizacije (19). Drugim riječima, nove tehnologije primijenjene u proizvodnji TEFBF-a i SDR-a mogu utjecati na SK neposredno nakon polimerizacije te na iznos i trajanje naknadnog porasta SK-a. Ovo upućuje na to da naknadna polimerizacija može trajati i dulje od uobičajeno prihvaćena 24 sata. Dodatno, svjetlosna aktivacija debljih slojeva može rezultirati nižim početnim SK-om u donjim dijelovima sloja (12) te naknadnom polimerizacijom većeg iznosa i duljeg trajanja.

Cilj ove studije bio je istražiti naknadnu polimerizaciju kompozita TEFBF i SDR na dubinama od 1 mm i 4 mm pri vremenima od 0 i 24 sata, te 7 i 30 dana. Nultim hipotezama pretpostavlja se nepostojanje razlike između:

- (I) vrijednosti SK-a između četiriju vremenskih točaka za zadani kompozit i dubinu;
- (II) iznos naknadne polimerizacije između dubina od 1 mm i 4 mm za zadani kompozit;
- (III) vrijednosti SK-a između kompozita i dubina unutar zadane vremenske točke.

within the 24 h after light curing (7-9). Although the literature does not explicitly claim that the post-cure polymerization ceases within 24 h, this is implicitly suggested by the design of numerous *in vitro* studies that are performed after an aging period of 24 h, which is considered sufficient to account for the changes in polymeric network structure due to the post-cure polymerization (7, 8, 10-13). The post-cure polymerization beyond 24 h has been scarcely investigated; only one study reported the DC increase after 30 days post-cure for composite samples that received lower radiant energies (14). Another study suggested the post-cure polymerization beyond 24 h by monitoring the gradual increase in hardness for up to 7 days (15).

A new generation of dental composites termed “bulk-fill” was recently introduced to the market and has been increasingly accepted due to a shortened and simplified clinical procedure. The bulk-fill composites are designed for placement in layers of 4-5 mm, opposite to conventional composites that enable maximum layer thickness of 2 mm. This is made possible by addressing two main factors that limited the composite layer thickness: polymerization shrinkage stress and low translucency (16, 17). The shrinkage stress is mitigated by lowering the elastic modulus (13), whereas the translucency is enhanced by lower filler ratio and larger particle size (17). Apart from these modifications, the fundamental chemistry of bulk-fill composites does not considerably differ from that of conventional composites. Their basis remains the photocurable blend of bifunctional methacrylate monomers and silanized glass fillers. However, there are some bulk-fill composites which exhibit innovative approaches for improving clinical performance. Namely, Tetric EvoFlow Bulk Fill (TEFBF) changes its translucency from 28% to 10% during polymerization in order to improve the esthetic appearance by mimicking the dentinal opacity (18). Another example is SDR that contains a proprietary modified urethane-dimethacrylate resin containing photoactive groups in order to control polymerization kinetics and retard the build-up of polymerization shrinkage stress (19). The aforementioned approaches may affect both the short term (during light curing) and long term (post-cure) polymerization behavior (19). In other words, the novel technologies employed in TEFBF and SDR may influence the DC immediately after curing, as well as the amount and duration of the post-cure DC increase. This means that the post-cure polymerization might last longer than 24 h, as commonly believed. Additionally, light curing of thick increments might cause lower initial DC of the bottom layer (12) and possibly a post-cure polymerization of higher extent or longer duration.

The aim of this study was to investigate the post-cure DC development of two composites TEFBF and SDR at depths of 1 mm and 4 mm at post-cure times of 0 h, 24 h, 7 d and 30 d. The null hypotheses assumed no difference in:

- (I) DC values among four post-cure time points for a given composite and depths;
- (II) post-cure DC increase between measuring depths of 1 mm and 4 mm for a given composite;
- (III) DC values between composites and depths within a given time point.

## Materijali i postupci

### Priprema uzoraka

Detaljni podatci o ispitanim *bulk-fill* kompozitima nalaze se u tablici 1. Četiri cilindrična uzorka ( $d = 3$  mm,  $h = 5$  mm) pripremljena su za svaki kompozit i mjernu dubinu s pomoću dvodijelnih kalupa od nehrđajućeg čelika. Nepolimerizirani kompozit postavljen je u kalup, otvori kalupa pokriveni su folijom od polietilena-tereftalata (PET) i materijal je svjetlosno aktiviran 20 sekunda kroz gornji otvor kalupa LED polimerizacijskim uređajem (Bluephase G2, Ivoclar-Vivadent, Schaan, Lihtenštajn) – raspon valnih duljina bio je od 380 do 515 nm, intenzitet  $1185$  mW/cm<sup>2</sup>, izmjereno integrirajućom sferom (IS, Gigahertz Optik GmbH, Puchheim, Njemačka). Vrh polimerizacijskog uređaja postavljen je izravno na PET foliju koja je prekrivala uzorak, a ambijentalna temperatura tijekom svjetlosne aktivacije bila je  $21 \pm 1$  °C. Ramanovi spektri prikupljeni su s dubina od 1 mm i 4 mm u četirima vremenskim točkama: 0 sati (neposredno nakon svjetlosne aktivacije), 24 sata, 7 dana i 30 dana, te su predstavljali ponavljana mjerenja na istim uzorcima. Između mjerenja uzorci su držani u mraku u inkubatoru (Cultura, Ivoclar-Vivadent, Schaan, Lihtenštajn) na temperaturi od  $37 \pm 1$  °C.

## Materials and methods

### Sample preparation

Detailed data on the investigated bulk-fill composites are shown in Table 1. Four cylindrical samples ( $d = 3$  mm,  $h = 5$  mm) were made for each composite as well as the measuring depth using a custom-made stainless steel split-mold. Uncured composite paste was placed into the mold, both mold apertures were covered with a polyethylene terephthalate (PET) film and curing was performed for 20 seconds through the upper aperture with the LED curing unit (Bluephase G2, Ivoclar-Vivadent, Schaan, Liechtenstein); wavelength range 380-515 nm, irradiance  $1185$  mW/cm<sup>2</sup>, as measured with integrating sphere (IS, Gigahertz Optik GmbH, Puchheim, Germany). The curing unit tip was positioned directly on top of the PET film covering the sample and the environmental temperature during curing was  $21 \pm 1$  °C. Raman spectra were collected from the depths of 1 mm and 4 mm at four time points: 0 h (immediately after light-curing), 24 h, 7 d and 30 d, representing repeated measurements on the same samples. The samples were dark stored in the incubator (Cultura, Ivoclar-Vivadent, Schaan, Liechtenstein) at  $37 \pm 1$  °C between the individual measurements at the mentioned time points.

**Tablica 1.** Podatci proizvođača o *bulk-fill* kompozitnim materijalima  
**Table 1** Information about the bulk-fill composite materials provided by manufacturers

Materijal (skraćena) • Material (abbreviation)	Proizvođač • Manufacturer	Nijansa / LOT / rok trajanja • Shade / LOT / exp.	Sastav • Composition	Punjenje • Filler load (wt%/vol%)
Tetric EvoFlow Bulk Fill (TEFBF)	Ivoclar Vivadent, Schaan, Liechtenstein	IVA / U34907 / 07/2017	Dimetakrilati • Dimethacrylates Barijevo staklo • Barium glass Iterbij trifluorid • Ytterbium trifluoride Kopolimeri • Copolymers	68/46
SDR (SDR)	Dentsply, York, PA, USA	universal / 1411000924 / 11/2016	Modificirani UDMA • Modified UDMA EBPADMA TEGDMA Ba–Al–F–B–Si–staklo • Ba–Al–F–B–Si–glass Sr–Al–F–Si–staklo • Sr–Al–F–Si–glass	68/45

UDMA = uretan dimetakrilat • urethane dimethacrylate, EBPADMA = etoksirani bisfenol-A-dimetakrilat • ethoxylated bisphenol-A-dimethacrylate, TEGDMA = trietilenglikol dimetakrilat • triethyleneglycol dimethacrylate

### Ramanova spektroskopija i analiza spektara

Kao što je već opisano, SK je izmjeren FT-Ramanovim spektroskopom *Spectrum GX* (PerkinElmer, Waltham, SAD) (5). Ukratko, Ramanovo raspršenje bilo je potaknuto laserom *NdYAG* (1064 nm) sa snagom od 400 mW. Spektri su prikupljeni s površine cilindričnih uzoraka na odabranim dubinama izlažući točku promjera 0,5 mm ekscitacijskom snopu. Spektralna rezolucija bila je  $4$  cm<sup>-1</sup> i za svaki spektar učinjeno je 50 skenova. Spektri nepolimeriziranih kompozita ( $n = 4$ ) prikupljeni su uz iste parametre. SK je izračunat kao relativna promjena intenziteta alifatske C = C vrpce na  $1640$  cm<sup>-1</sup> normaliziran prema aromatskoj C = C vrpci na  $1610$  cm<sup>-1</sup>, prema sljedećoj formuli:  $DC = 1 - R_{\text{polimerizirano}} / R_{\text{nepolimerizirano}}$ , gdje je R = (visina alifatske C = C vrpce) / (visina aromatske C = C vrpce).

### Raman spectroscopy and spectra analysis

A FT-Raman spectrometer *Spectrum GX* (PerkinElmer, Waltham, USA) was used for DC evaluation, as previously described (5). Briefly, Raman scattering was induced by an *NdYAG* laser (1064 nm) with power of 400 mW. The spectra were collected from the surface of cylindrical samples at selected depths by exposing the spot of 0.5 mm in diameter to the excitation beam. The spectral resolution was  $4$  cm<sup>-1</sup> and 50 scans were taken for each spectrum. The spectra of the uncured composites ( $n=4$ ) were collected using the same parameters. DC was calculated as the relative intensity change of the aliphatic C=C band at  $1640$  cm<sup>-1</sup> normalized to the aromatic C=C band at  $1610$  cm<sup>-1</sup>, according to the equation:  $DC = 1 - R_{\text{polymerized}} / R_{\text{unpolymerized}}$ , where R = (aliphatic C=C peak height) / (aromatic C=C peak height).

## Statistička analiza

Podatci su bili normalno distribuirani i zato su prikazani kao srednje vrijednosti  $\pm$  standardne devijacije. Srednje vrijednosti SK-a uspoređene su mješovitim modelom ANOVA-e, pri čemu su *materijal* i *dubina* bili čimbenici između subjekata, a *vrijeme* čimbenik unutar subjekata. Parcijalnom eta-kvadrat statistikom određen je relativni učinak čimbenika i njihove interakcije. Višestruke usporedbe provedene su s pomoću Tukeyeve HSD i Bonferronijeve prilagodbe za nezavisna i zavisna opažanja. Statistička analiza obavljena je softverom SPSS 20 (IBM, Armonk, NY, SAD) uz  $\alpha = 0,05$ .

## Rezultati

Srednje vrijednosti SK-a i rezultati statističke analize nalaze se na slici 1., a mjera veličine učinka (vrijednosti parcijalnih eta-kvadrata) u tablici 2. Vrijednosti SK-a izmjerene su u rasponu od 61,3 do 81,1 posto za TEFBF i od 58, do 81,6 posto za SDR. Početni (0 sati) SK za oba materijala (4,9 % za SDR i 11,1 % za TEFBF) bio je značajno niži na dubini od 4 mm negoli od 1 mm.

Statistički značajna interakcija zapažena je za čimbenike *vrijeme*\**materijal* i *vrijeme*\**dubina*, što upućuje na razlike u naknadnom porastu SK-a između materijala i mjernih dubina. Stoga je učinak čimbenika *vrijeme* i *dubina* analiziran za svaki materijal posebno (tablica 2.). Oba kompozita pokazala su značajan učinak čimbenika *vrijeme* i *dubina*, s većim učinkom čimbenika *vrijeme*. Dodatno, TEFBF je pokazao značajnu interakciju čimbenika *vrijeme* i *dubina*, što upućuje na razliku u naknadnom razvoju SK-a između dubina od 1 mm i 4 mm.

Za oba materijala zabilježen je značajan naknadni porast SK-a u maksimalnom iznosu od 16,4 posto za TEFBF i 20,6 posto za SDR. Na dubini od 4 mm SDR je pokazao statističku heterogenost vrijednosti SK-a pri vremenima od 0 i 24 sata te 7 dana, a to upućuje na to da naknadni porast SK-a može biti detektiran do sedam dana nakon svjetlosne aktivacije. Također za SDR na dubini od 1 mm, zapažen je trend porasta SK-a do 7 dana, no nije bio statistički značajan.

Oba kompozita su 30 dana nakon svjetlosne aktivacije dosegla visoke vrijednosti SK-a – u rasponu od 76,1 do 81,6 posto – unatoč značajnim početnim razlikama. Vrijednosti SK-a, kad je riječ o vremenima od 7 i 30 dana, bile su statistički slične za oba materijala i obje mjerne dubine.

## Statistical analysis

Since the data were normally distributed, they were summarized as mean values  $\pm$  standard deviations. Mean DC values were compared by a mixed model ANOVA, with “material” and “depth” as the between-subject factors and “time” as the within-subject factor. Partial eta-squared statistics was used to assess the relative influences of the factors and their interactions. Multiple comparisons were performed using Tukey’s HSD and Bonferroni adjustments for independent and dependent observations, respectively. Statistical analysis was performed in SPSS 20 (IBM, Armonk, NY, USA) with  $\alpha=0.05$ .

## Results

Mean DC values and results of statistical analysis are shown in Figure 1, whereas measures of effect size (partial eta-squared values) are shown in Table 2. The DC values ranged from 61.3-81.1% for TEFBF and 58.9-81.6% for SDR. The initial (0 h) DC was significantly lower at the depth of 4 mm than at the depth of 1 mm for both materials (4.9% for SDR and 11.1% for TEFBF).

A statistically significant interaction was observed for the factors time\*material and time\*depth, indicating differences in post-cure DC increase between the materials and measuring depths. Hence, the influence of the factors “time” and “depth” was analyzed for each material separately (Table 2). Both composites showed a significant influence of the factors “time” and “depth”, with higher influence of the factor “time”. Additionally, TEFBF showed a significant interaction of the factors “time” and “depth”, indicating that the post-cure development of DC differed between the measuring depths of 1 mm and 4 mm.

Both materials presented a significant post-cure DC increase, amounting up to 16.4% for TEFBF and 20.6% for SDR. At the depth of 4 mm, SDR also showed a statistical heterogeneity of DC values at 0 h, 24 h and 7 d, indicating that the post-cure DC increase could be detected for up to 7 days post-cure. Also, for SDR at 1 mm depth, a non-significant trend of DC increase for up to 7 days was observed.

Both TEFBF and SDR at 30 days post-cure presented high DC values ranging between 76.1-81.6%, despite the significant initial differences. The DC values reached at time points of 7 d and 30 d were statistically similar for both materials at both measuring depths.

**Tablica 2.** Učinak čimbenika: vrijeme, materijal i dubina te njihove interakcije na stupanj konverzije  
**Table 2** Influence of different factors: time, material and depth and their interactions on the degree of conversion

Materijal • Material	Čimbenik • Factor	p	Djelomični $\eta^2$ • Partial $\eta^2$
Ukupno • Overall	Vrijeme • Time	<0.001	0.939
	Materijal • Material	N.S.	-
	Dubina • Depth	<0.001	0.657
	Materijal * dubina • Material * depth	N.S.	-
	Vrijeme * materijal • Time * material	<0.001	0.495
	Vrijeme * dubina • Time * depth	0.004	0.308
TEFBF	Vrijeme • Time	<0.001	0.910
	Dubina • Depth	0.013	0.671
	Vrijeme * dubina • Time * depth	0.006	0.487
SDR	Vrijeme • Time	<0.001	0.957
	Dubina • Depth	0.008	0.717
	Vrijeme * dubina • Time * depth	N.S.	-

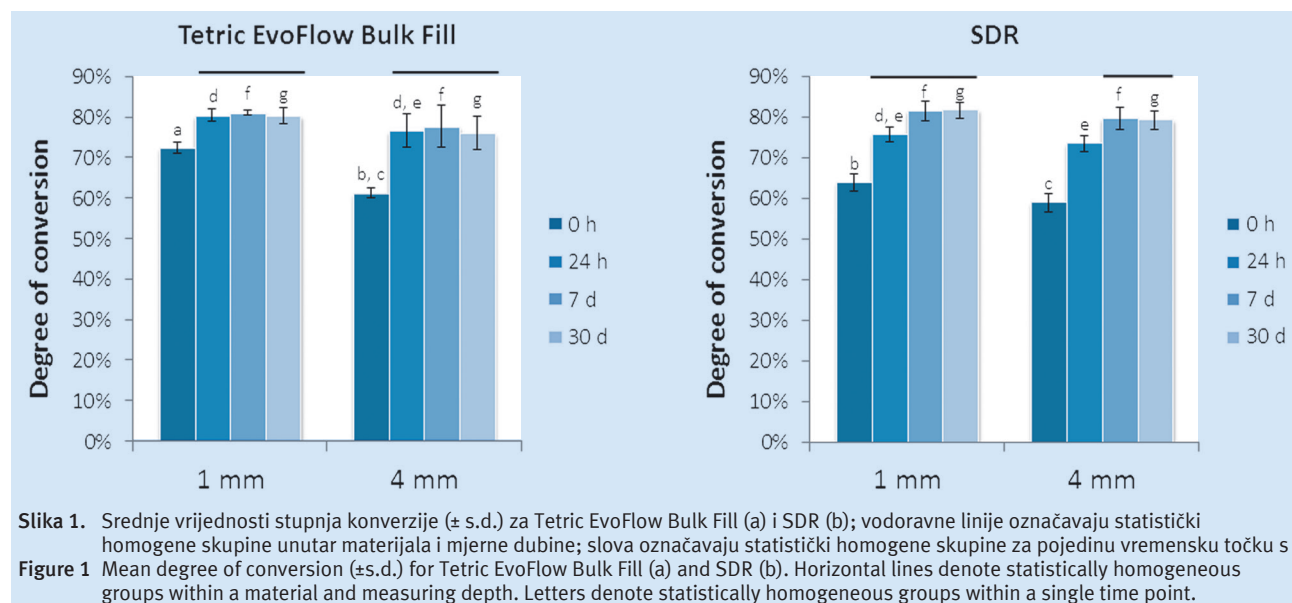
N.S. = nije značajno • not significant

## Rasprava

U ovoj studiji istražen je dugoročni naknadni porast SK-a pri uporabi dvaju *bulk-fill* kompozita na dvije dubine. Prva je nulta hipoteza odbačena jer su vrijednosti SK-a s vremenom rasle, kad je riječ o oba materijala i obje dubine. Usporedbom naknadnoga porasta SK-a za pojedini materijal i dubinu može se uočiti da je TEFBF dosegnuo maksimum nakon 24 sata na obje mjerne dubine, a za SDR zabilježen je značajan porast SK-a na dubini od 4 mm čak do 7 dana nakon svjetlosne aktivacije (slika 1.). To pokazuje da je dubljim slojevima SDR-s

## Discussion

This study investigated a long term DC development of two bulk-fill composites at two depths. The first null hypothesis was rejected, since the DC values increased with time for both materials and depths. By comparing the post-cure DC increase within a single material and depth, it can be seen that TEFBF reached the DC plateau after 24 h at both measuring depths, while SDR showed a significant DC increase for up to 7 days post-cure at 4 mm depth (Figure 1). This suggests that deeper layers of SDR need longer times than the com-



potrebno dulje od uobičajeno prihvaćena 24 sata (7, 8, 12) kako bi dosegli konačni SK. Produžena naknadna polimerizacija pri promjeni SDR-a može se pripisati modificiranom uretan-dimetakrilatu s ugrađenim fotoaktivnim skupinama kao strategiji za usporavanje razvoja polimerizacijskog stresa s pomoću kontrole polimerizacijske kinetike (19). U uputama proizvođača to je nazvano *polimerizacijskim modulatorom* koji favorizira linearni rast lanaca umjesto umrežavanja (20). Takvo kinetičko ponašanje dopušta više viskoznog protoka omogućujući smanjenje polimerizacijskog stresa tijekom polimerizacije SDR-a (19). Nuspojava polimerizacijskog modulatora mogla bi biti usporena kinetika konverzije, što može rezultirati produljenom naknadnom polimerizacijom. Također, najvjerojatnije, niža gustoća umrežavanja može dopustiti veću pokretljivost reaktivnih spojeva (21) i tako dodatno poduprijeti produljenu naknadnu polimerizaciju. Trend naknadnog porasta SK-a do 7 dana zapažen je pri uporabi SDR-a i na dubini od 1 mm, ali bez statističke značajnosti. Nemoćnost ove analize da otkrije statističku značajnost mogla bi se pripisati nižem iznosu naknadne polimerizacije na dubini od 1 mm zbog većega početnog SK-a. Kako je atenuacija polimerizacijskog svjetla bila znatno manja na dubini od 1 mm negoli na 4 mm (22), više je monomera potrošeno tijekom svjetlosne aktivacije pa ga je manje ostalo za naknadnu polimerizaciju (23).

monly accepted 24 h (7, 8, 12) to attain their final DC. The prolonged post-cure polymerization found in SDR may be attributed to its modified urethane dimethacrylate that incorporates photoactive groups as a strategy to decrease shrinkage stress development through controlling of the polymerization kinetics (19). In the manufacturer brochures, this is referred to as a "polymerization modulator" and is claimed to favor linear chain growth instead of crosslinking (20). Such behavior allows for more viscous flow and acts to decrease the shrinkage stress during polymerization of SDR (19). The side-effect of the polymerization modulator might have been the retardation of conversion kinetics, resulting in extended post cure polymerization. Also, the presumably lower crosslinking density of the polymeric network might allow better mobility of reactive species (21) thus supporting the prolonged post-cure polymerization. The trend of post-cure DC increase for up to 7 days was also observed for SDR at 1 mm depth, but there was no statistical significance. The inability of our analysis to detect statistical significance could be attributed to the lower extent of post-cure polymerization occurring at 1 mm depth, due to higher initial DC. Since the curing light was much less attenuated at the depth of 1 mm than at 4 mm (22), more monomers were consumed during light-curing and thus lower amount of monomers was left for the subsequent post-cure polymerization (23).

Statistička analiza pokazala je značajnu interakciju između čimbenika *vrijeme* i *dubina* pri uporabi TEFBF-a (tablica 2.), što upozorava da je razvoj SK-a tijekom vremena bio različit između dubina od 1 mm i 4 mm, zbog čega je u slučaju TEFBF-a odbačena druga nulta hipoteza. Navedena razlika najvećim je dijelom uzrokovana nižim početnim SK-om i višim iznosom naknadne polimerizacije na dubini od 4 mm (slika 1. a). Zbog atenuacije svjetla koje prolazi kroz materijal zbog apsorpcije i raspršenja na česticama punila (22), dubina od 4 mm primila je nižu energiju zračenja. Prema Lambert-Beerovu zakonu intenzitet svjetla smanjuje se eksponencijalno s duljinom optičkoga puta (24). Stoga se broj aktiviranih molekula fotoinicijatora smanjuje s porastom debljine sloja, što se odražava kao značajno niži početni (0 sati) SK (61,3 %) na 4 mm negoli na 1 mm (72,4 %). Ta razlika ujednačena je nakon 24 sata (slika 1. a) te upućuje na to da je energija zračenja koja je dosegla 4 mm omogućila naknadnu polimerizaciju dostatnu da kompenzira početno niži SK. To je moguće jer se metakrilat polimerizira s pomoću slobodno-radikalne adicijske reakcije u kojoj radikal na kraju polimernog lanca ostaje sačuvan tijekom propagacije (25). Zato pojedinačan slobodni radikal može potaknuti adiciju velikog broja monomernih jedinica prije nego što ga inaktivira terminacija ili ograničena pokretljivost. Dapače, doseg polimerizacije u punjenim metakrilatnim smolama primarno je određen ograničenom pokretljivošću uzrokovanom enormnim porastom viskoznosti, a ne trošenjem reaktanata (26). Zato broj slobodnih radikala nije glavni ograničavajući čimbenik za doseg polimerizacije, čemu u prilog govori i njihova prisutnost nakon završetka polimerizacije (4). Ovime se mogu objasniti rezultati pri uporabi TEFBF-a koji pokazuju da je količina slobodnih radikala na dubini od 4 mm bila dostatna za postizanje statistički sličnog SK-a kao i na 1 mm, unatoč značajnim početnim razlikama.

Za razliku od TEFBF-a, SDR je pokazao sličan naknadni porast SK-a na dubinama od 1 mm i 4 mm, na što upućuje nepostojanje značajne interakcije između čimbenika *vrijeme*\**dubina* (tablica 2.). Zato je za SDR prihvaćena druga nulta hipoteza. Čini se da su visok intenzitet polimerizacijskog svjetla (1185 mW/cm<sup>2</sup>) i 20-sekundna svjetlosna aktivacija, u kombinaciji s visokom translucencijom SDR-a (17), aktivirali dostatan broj molekula fotoinicijatora koji je doveo do statistički slične brzine konverzije na obje dubine. Dodatno, translucencija SDR-a povećava se tijekom polimerizacije zbog smanjenja razlike u indeksima loma između smole i čestica punila te posljedičnog smanjenja raspršenja svjetlosti (17). To poboljšava učinkovitost svjetlosne aktivacije na većim dubinama jer svjetlosna transmisija kroz gornje dijelove sloja raste dok polimerizacija napreduje.

Iako su početne (0 sati) vrijednosti SK-a bile značajno niže na 4 mm negoli na 1 mm za oba kompozita, razlika pri uporabi SDR-a (4,9 %) bila je dvostruko manja negoli za TEFBF (11,1%). Mogući uzrok je veća translucencija SDR-a (17) i jedinstven obrazac promjene translucencije pri korištenju TEFBF-a (18). TEFBF sadržava patentiranu tehnologiju precizno usklađenih indeksa loma smole i čestica punila koja omogućuje visoku translucenciju nepolimeriziranog materijala (28 %) i njezino postupno smanjenje tijekom polimeriza-

Statistical analysis showed a significant interaction between the factors “time” and “depth” for TEFBF (Table 2), indicating that the development of DC through time was different between depths of 1 mm and 4 mm, thus leading to rejection of the second null-hypothesis in the case of TEFBF. This difference is mostly caused by lower initial DC and higher extent of post-cure polymerization at the depth of 4 mm (Figure 1a). The light passing through the material is attenuated due to absorption and scattering at filler particles (22), hence the depth of 4 mm received lower radiant energy. According to the Lambert-Beer law, the light intensity decreases exponentially with length of the light path (24). As a result, the number of activated photoinitiator molecules is diminished as the layer thickness increases, reflecting in significantly lower initial (0 h) DC (61.3%) at 4 mm, compared to that at 1 mm (72.4%). However, this difference was leveled after 24 h (Figure 1a), suggesting that the radiant energy delivered to 4 mm enabled sufficient extent of post-cure polymerization to compensate for initially lower DC. This is possible because the methacrylate polymerization occurs via free-radical addition reaction that preserves a free radical at the end of polymeric chain throughout the propagation (25). In this way, a single free radical can trigger addition of a large number of monomer units before it becomes inactivated by termination or mobility restrictions. In fact, the extent of polymerization in filled dimethacrylate resins is mainly determined by mobility restrictions caused by an enormous increase in viscosity rather than the depletion of reactants (26). Therefore, the number of free radicals is not the main limiting factor for extent of polymerization, as evidenced by their persistence after the end of polymerization (4). This may explain our results for TEFBF, which showed that the amount of free radicals at 4 mm depth was sufficient to attain statistically similar post-cure DC to that at 1 mm depth, despite the significant initial differences.

In contrast to TEFBF, SDR showed similar post-cure DC development at depths of 1 mm and 4 mm, as indicated by no significant interaction of factors time\*depth (Table 2). Therefore, the second null-hypothesis was accepted for SDR. It appears that the high intensity of curing light (1185 mW/cm<sup>2</sup>) and curing time of 20 seconds combined with high translucency of SDR (17) activated enough photoinitiator molecules to result in statistically similar post-cure conversion rate at both depths. Additionally, the translucency of SDR increases during polymerization due to the decrease of refractive index mismatch between the resin and filler particles and a consequent decline of light scattering (17). This facilitates curing efficiency at higher depths, since the light transmission through the overlying layers improves as they are cured.

Although the initial (0 h) DC values were significantly lower at 4 mm than at 1 mm for both composites, the difference for SDR (4.9%) was twice lower than that of TEFBF (11.1%). This may have been caused by high translucency of SDR (17), as well as a unique translucency change of TEFBF (18). TEFBF contains a patented technology of finely tuned refractive indices of resin and filler particles, allowing for high translucency of the uncured paste (28%) that progressively

cije do vrijednosti od oko 10 posto (18). Taj prijelaz s visoke na nisku translucenciju omogućuje učinkovit prodor svjetlosti tijekom početne faze svjetlosne aktivacije i estetski izgled konačne restoracije zbog niske translucencije polimeriziranog materijala. Pritom se TEFBF ponaša suprotno od većine komercijalnih kompozita (uključujući SDR) kojima se translucencija povećava tijekom svjetlosne aktivacije (27, 28). Kako su gornji dijelovi uzoraka pri uporabi TEFBF-a primili veći intenzitet polimerizacijske svjetlosti negoli oni dublji, u njima se dogodilo sniženje translucencije i posljedično jača atenuacija svjetla koje dopire do dubine od 4 mm. Ovim se može objasniti razmjerno velika razlika u SK-u između dubina od 1 mm i 4 mm u slučaju TEFBF-a. Ipak, unatoč početno nižem SK-u na dubini od 4 mm, naknadna polimerizacija poništila je razliku i rezultirala statistički sličnim SK-om između dubina od 1 mm i 4 mm pri svim vremenima nakon svjetlosne aktivacije (24 sata, 7 dana i 30 dana).

S obzirom na početne (0 sati) vrijednosti SK-a na dubini od 1 mm, TEFBF je pokazao značajno više vrijednosti negoli SDR. Početni SK određen je kompleksnim međudjelovanjem velikog broja parametara, kao što su struktura, reaktivnost i relativne količine monomera (25), udjel i geometrija čestica punila (29, 30), kemijski sastav fotoinicijatora (31) i patentirani aditivi neotkrivena sastava (18, 19). Zato izravna usporedba vrijednosti SK-a između TEFBF-a i SDR-a ne daje mnogo informacija o cjelokupnoj izvedbi materijala. Izolirani podatak o SK-u nedostatan je za usporedbu svojstava ovisnih o SK-u između različitih formulacija, jer na svojstva znatno utječu i mnogobrojni drugi čimbenici (32). Ipak, zanimljivo je to što su oba kompozita, svaki sa svojim patentiranim modifikacijama i različitim početnim vrijednostima SK-a, konvergirali prema statistički sličnim vrijednostima SK-a na obje dubine sedam dana nakon svjetlosne aktivacije (slika 1.). Zato je treća nulta hipoteza prihvaćena za vremena nakon svjetlosne aktivacije od 7 dana i 30 dana. To pokazuje da oba kompozita imaju sličan *maksimalno ostvariv* SK, a došuju ga u određenom vremenu nakon svjetlosne aktivacije, neovisno o početnim vrijednostima SK-a i razlikama u brzini polimerizacije. Konačan SK vjerojatno je bio određen pokretljivošću reaktivnih spojeva koji je pod utjecajem udjela (29) geometrije i površinskog tretmana (33) čestica punila, te viskoznosti smole (34). O ovome se ne može raspravljati jer je proizvođač samo djelomice otkrio podatke o sastavu (tablica 1.). Budući da oba kompozita sadržavaju udjel punila od 45 vol%, može se nagađati da je ovaj parametar bio presudan za njihove konačne vrijednosti SK-a (29, 30), a ostali čimbenici vjerojatno su bili manje važni. Alternativno objašnjenje jest da su ostali čimbenici koji utječu na SK u oba kompozita bili slični.

Tijekom cijele polimerizacije multifunkcionalnih metakrilata, reakcija ciklizacije natječe se s umrežavanjem (35), a ovo drugo postaje dominantno s napretkom polimerizacije. Zato čak i mali porast SK-a u kasnijim fazama polimerizacije može znatno povećati gustoću umreženosti polimera (26, 36). Iako je porast SK-a koji je nastupio pri uporabi SDR-a nakon 24 sata bio malen u usporedbi sa SK-om ostvarenim tijekom prva 24 sata nakon svjetlosne aktivacije (oko 6 % prema 75 %), zabilježeno poboljšanje SK-a ipak može povoljno utjecati na ostala svojstva, poglavito na ona koja ovise

decreases during polymerization to about 10% (18). The transition from high to low translucency allows high light penetration during the initial phase of light curing and an esthetic appearance due to low translucency of a cured restoration. In this regard, TEFBF behaves opposite to most of the commercial composites (including SDR), whose translucency increases during curing (27, 28). Since the upper parts of the TEFBF samples received higher irradiance than deeper layers, they underwent the translucency decrease and consequently attenuated the light delivered to the 4 mm depth. This could explain the relatively large DC difference between the depths of 1 mm and 4 mm in the case of TEFBF. However, despite the 4 mm depth exhibited an initially lower DC, the post-cure polymerization completely negated the difference, yielding statistically similar DC values between 1 mm and 4 mm at all post-cure times (24 h, 7 d and 30 d).

Considering the initial (0 h) DC values at 1 mm depth, TEFBF showed significantly higher values than SDR. The initial DC is determined by a complex interplay of multiple parameters such as structure, reactivity and relative amounts of monomers (25), filler load and geometry (29, 30), photoinitiator chemistry (31) and proprietary undisclosed additives (18, 19). In consequence, the direct comparison of DC values between TEFBF and SDR does not provide much indication of the overall material performance. The DC data alone are insufficient to compare the DC-dependent properties among different formulations, since these properties are considerably influenced by a number of other factors (32). However, it is interesting to note that these two composites, each with its own proprietary modifications and different initial DC values, managed to converge to statistically similar DC values at both depths after 7 days post-cure (Figure 1). Therefore, the third null hypothesis was accepted for post-cure times of 7 d and 30 d. This suggests that both composites have similar "maximum attainable" DC, that is reached after a certain post-cure time, irrespective of the initial DC values and differences in polymerization rate. This final DC was probably determined by the mobility of unreacted species, which was influenced by filler load (29), geometry and surface treatment (33), as well as resin viscosity (34). This cannot be discussed into detail, since the compositional information is only partially disclosed (Table 1). As both composites contain filler load of about 45 vol%, it could be speculated that it was the major determinant of final DC values (29, 30), while other factors were probably less important. Also, an alternative explanation is that other DC-determining factors might have been similar in both composites.

Throughout the polymerization of multifunctional methacrylates, the cyclization competes with crosslinking (35) and the latter becomes dominant as the polymerization advances. Thus, even a small DC increase at late phases of polymerization might considerably enhance the crosslinking density of a polymeric network (26, 36). Despite the DC improvement that occurred in SDR beyond 24 hours was small relative to the DC attained within the first 24 h post-cure (about 6% and 75%, respectively), it may favorably reflect on other material properties, mainly those dependent upon crosslinking, i.e. mechanical properties (26), water sorption, degrada-



o umreženosti, tj. na mehanička svojstva (26), apsorpciju vode, degradaciju u vodenom mediju i otpuštanje topljivih sastojaka (37).

Ovo istraživanje pokazalo je da neke kemijske modifikacije, koje se pojavljuju tijekom uporabe *bulk-fill* kompozita, mogu uzrokovati produljeni naknadni porast SK-a čak do 7 dana. Materijali TEFBF i SDR izabrani su zato što sadržavaju nove tehnologije koje se ne nalaze u sastavu ostalih komercijalnih kompozita. Dobiveni rezultati ne smiju se generalizirati i primijeniti na cijelu skupinu *bulk-fill* kompozita jer svaki materijal ima drukčiji sastav i jedinstvene modifikacije koje mu omogućuju postavljanje u debljem sloju. Potrebno je napomenuti da navedene modifikacije mogu utjecati i na druga važna svojstva materijala i zato se njihovi učinci trebaju dodatno istražiti.

## Zaključci

Nalaz produljene naknadne polimerizacije ima dvije glavne implikacije, a prva je laboratorijska. Naime, istraživanja svojstava ovisnih o SK-u možda je potrebno provesti poslije uobičajeno prihvaćenih 24 sata nakon svjetlosne aktivacije, jer se svojstva nekih *bulk-fill* kompozita mogu nastaviti razvijati i nakon tog vremena. Drugo, dugotrajnija naknadna polimerizacija upućuje na mobilnost i dostupnost reaktivnih spojeva koji mogu biti otpušteni u usnu šupljinu tijekom duljeg razdoblja, s mogućim učincima na biokompatibilnost.

## Zahvala

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## Sukob interesa

Autori nisu bili u sukobu interesa.

tion in aqueous environment and release of leachable components (37).

This study demonstrated that some of the chemistries used in bulk-fill composites might cause prolonged post-cure DC increase of up to 7 days. The materials TEFBF and SDR were chosen because they feature two novel technologies that are not contained in other commercial composites. Our findings must not be generalized. They should not be applied to the whole class of bulk-fill composites because each material features different composition and unique modifications to achieve the bulk-fill capability. However, these modifications may inadvertently affect other important material properties; hence their effects should be further investigated.

## Conclusions

The finding of prolonged post-cure polymerization has two main implications. First, the post-cure times at which the DC-dependent composite properties are tested in laboratory setting may need to be longer than the commonly accepted 24 hours since the properties of some bulk-fill composites may develop beyond this time. Second, the longer post-cure polymerization suggests that reactive species are mobile and available for leaching into the oral environment during an extended time period, which raises biocompatibility concerns.

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## Conflict of interest

The authors declare no conflict of interest.

## Abstract

**Objectives:** To investigate the long-term development of the post-cure degree of conversion (DC) for two flowable bulk-fill composites. **Materials and methods:** Tetric EvoFlow Bulk Fill (TEFBF) and SDR were chosen due to their distinct compositional modifications that enable the decrease of translucency during polymerization and lower polymerization rate, respectively. DC was assessed using FT-Raman spectroscopy at the post-cure times of 0 h, 24 h, 7 d and 30 d. The post-cure behavior was analyzed by a mixed model ANOVA and partial eta-squared statistics. **Results:** DC ranged from 61.3-81.1% for TEFBF and 58.9-81.6% for SDR. The initial (0 h) DC was significantly lower at a depth of 4 mm than at a depth of 1 mm (4.9% for SDR and 11.1% for TEFBF). Both materials presented a significant post-cure DC increase, up to 16.4% for TEFBF and 20.6% for SDR. The post-cure DC development was depth-dependent for TEFBF, but not for SDR. The post-cure DC increase was observed during 24 h for TEFBF and 7 d for SDR. **Conclusions:** Some of the bulk-fill composites may need longer times than the commonly accepted 24 h to reach the final conversion. This may be attributed to their compositional modifications that are mostly undisclosed by manufacturers. Our findings imply that investigations commonly performed 24 h post-cure may underestimate some of the bulk-fill composite properties, if these are affected by the slowly-developing DC. Reactive species may also be available for leaching out of the restoration during an extended time period, with possible implications on biocompatibility.

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## Address for correspondence

Matej Par  
Private Dental Practice  
Dankovecka 9, 10000 Zagreb, Croatia  
mpar@inet.hr

## Key words

Composite Resins; Polymerization; Spectrum Analysis, Raman

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